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## MEANS FOR REMOVING UNWANTED IONS FROM AN ION TRANSPORT SYSTEM AND MASS SPECTROMETER

This application is a continuation of and claims priority to U.S. application Ser. No. 09/787,358, filed on May 15, 2001, which is the National Stage of International Application PCT/GB99/03076, filed on Sep. 16, 1999, the entire disclosure of which is incorporated by reference.

### FIELD OF THE INVENTION

The present invention relates to inductively coupled plasma mass spectrometry (ICPMS). However, the concepts can be applied to any type of mass spectrometer which generates unwanted artefact ions as well as ions of analytical significance, such artefact ions having properties that allow them to be selectively removed from the ion beam by causing them to interact with a reagent gas whilst the ions of analytical significance are substantially retained in the beam.

### BACKGROUND OF THE INVENTION

The general principles of ICPMS are well known. It is a method of elemental analysis providing information about the elemental composition of a sample, with little or no information about its molecular structure. Typically, the sample is a liquid, which is nebulised and then passed through an electrically-maintained plasma, in which the temperature is high enough to cause atomization and ionisation of the sample. Typically temperatures greater than 5000K are used. The ions produced are introduced, via one or more stages of pressure reduction, into a mass analyser. The mass analyser is most commonly a quadrupole, although magnetic sector analysers are also used and, more recently, time-of-flight devices.

A problem common to all of these, although most troublesome in low-resolution devices such as quadrupoles, is the presence in the mass spectrum of unwanted artefact ions that impair the detection of some elements. The identity and proportion of artefact ions depends upon the chemical composition of both the plasma support gas and that of the original sample. There are many such artefact ions. Typical are argon-containing molecular ions that are encountered in argon-based ICPMS, which is the most wide-spread technique. Argon oxide ( $\text{ArO}^+$ ) and argon dimer ( $\text{Ar}_2^+$ ) are prominent, and interfere with the detection of iron ( $^{56}\text{Fe}$ ) and selenium ( $^{80}\text{Se}$ ) respectively. An example of a troublesome atomic ion is  $\text{Ar}^+$ , which interferes with the detection of  $^{40}\text{Ca}$ .

A collision cell may be used to remove unwanted artefact ions from an elemental mass spectrum. The use of a collision cell is described in EP 0 813 228 A1, WO 97/25737 and U.S. Pat. No. 5,049,739.

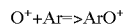
A collision cell is a substantially gas-tight enclosure through which ions are transmitted. It is positioned between the ion source and the main spectrometer. A target gas is admitted into the collision cell, with the objective of promoting collisions between ions and the neutral gas molecules or atoms. The collision cell may be a passive cell, as disclosed in U.S. Pat. No. 5,049,739, or the ions may be confined in the cell by means of ion optics, for example a multipole which is driven with a combination of alternating and direct voltages, as in EP 0 813 228. By this means the collision cell can be configured so as to transmit ions with minimal losses, even when the cell is operated at a pressure that is high enough to guarantee many collisions between the ions and the gas molecules.

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By careful control of the conditions in the collision cell, it is possible to transmit the wanted ions efficiently. This is possible because in general the wanted ions, those that form part of the mass spectrum to be analyzed, are monatomic and carry a single positive charge; that is, they have "lost" an electron. If such an ion collides with a neutral gas atom or molecule, the ion will retain its positive charge unless the first ionisation potential of the gas is low enough for an electron to transfer to the ion and neutralise it. Consequently, gases with high ionisation potentials are ideal target gases.

Conversely, it is possible to remove unwanted artefact ions whilst continuing to transmit the wanted ions efficiently. For example the artefact ions may be molecular ions such as  $\text{ArO}^+$  or  $\text{Ar}_2^+$  which are much less stable than the atomic ions. In a collision with a neutral gas atom or molecule, a molecular ion may dissociate, forming a new ion of lower mass and one or more neutral fragments. In addition, the collision cross section for collisions involving a molecular ion tends to be greater than for an atomic ion. This was demonstrated by Douglas (Canadian Journal Spectroscopy, 1989 vol 34(2) pp 38-49). Another possibility is to utilise reactive collisions. Eiden et al (Journal of Analytical Atomic Spectrometry vol 11 pp 317-322 (1996)) used hydrogen to eliminate many molecular ions and also  $\text{Ar}^+$ , whilst analyte ions remain largely unaffected.

However, when the collision cell is operated at a pressure that is sufficiently high to promote removal of the artefact ions that originate in the plasma, other artefact ions may form. The chemical nature of these ions is not always known with certainty, but, for example, hydrocarbons that are present in the residual gas composition may be ionised by charge exchange. Various species of metal oxide and/or hydroxide ions such as  $\text{LaO}^+$  and  $\text{LaOH}^+$  have been observed, apparently formed in ion-molecule reactions in the cell water adduct ions such as  $\text{LaO} \cdot \text{H}_2\text{O}^+$  have also been observed. The artefact ions that are removed in the collision cell can also be generated there, for example by reactions such as:



so that the extent to which such ions are removed from the beam will depend on the equilibrium of two or more reaction pathways.

Even when no collision gas is being admitted to the cell, the local pressure in the cell can be quite high, due to the gas load from the plasma itself. The gas load from the plasma is composed primarily of the plasma support gas, and so is generally neutral argon. The gas load from the plasma consists of a directed flow, which is carried with the ion beam, and a general back pressure in the evacuated chamber through which the ion beam passes. The gas load from the plasma will also contain other species, typically hydrogen and oxygen if the sample is dissolved in water, and probably organics, for example from rotary pump oil from the expansion chamber, which is the coarse vacuum stage commonly employed in ICPMS as the first stage of pressure reduction.

The present inventors have used a calculation similar to that described by Douglas and French (1988) to estimate the gas load on a collision cell in a typical prior art mass spectrometer. This calculation suggests that the local partial pressure in the cell due to the gas load from the plasma can be 0.001 mbar or even greater, especially if the collision cell is close to the ion source. Using a capillary connected to a capacitance manometer to measure the stagnation pressure in the sampled beam, the present inventors have found that with the probe on axis and 42 mm from the skimmer, a